CORRELATION OF THE FLOW PROPERTIES OF COLLOIDAL SOLUTIONS WITH A SOL-GEL FILM STRUCTURE

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The variation in the viscosity and surface tension of film-forming solutions of $CuO - TiO_2$ and $Bi_2O_3 - Fe_2O_3 - TiO_2$ systems in accordance with the variations in their composition and the type of material is analyzed. The correlation of the viscosity and surface tension with the proportion by volume and the surface area of disperse phase is elucidated. The correlation of the viscosity and surface tension with the solvent type, shape of sol particles, and film microstructure is evaluated.

The present paper correlates the structural transformations of two-component ($CuO - TiO_2$ system) and three-component ($Bi_2O_3 - Fe_2O_3 - TiO_2$ system) films with the viscosity and surface tension of the film-forming solutions (FFS) used to produce these films.

The investigation was carried out on five two-component and seven three-component solutions differing either in the $CuO : TiO_2$ and $Bi_2O_3 : TiO_2$ ratios in the films or in the materials used to prepare the solutions.

The titanium component was represented by tetra-alkoxides (titanium tetraethoxide (TET) and titanium tetra-n-butoxide (TBT) which are good in forming of films. The main requirement imposed on the materials containing copper, bismuth, and iron consisted in solubility in the alcohols used in these processes [1]. Copper, bismuth, and iron chlorides and copper nitrate were the preferred materials. The acids analogous to the anions of the salts listed were used as the catalyst of hydrolysis of titanium alkoxides, and ethanol acted as the solvent. Thus, the FFS was an aqueous-alcohol solution of titanium tetraalkoxide hydrolyzate and cupric salts or bismuth and iron chlorides.

The total mass content of the components converted into oxides (FFS concentration) was 5%. The solution viscosity was determined by the capillary method using a VPZh-1 viscosimeter and the surface tension was determined by the falling drop method.

The samples of thermally ground glass sheet were placed in the FFS and extracted at a constant rate of 1 mm/sec, then held at room temperature in air to complete hydrolysis and polycondensation processes, as well as for drying and primary solidification of the film. For final fixation and strengthening, the coating film was heat-treated in a furnace

equipped with silit heaters at 450°C for 30 min. All measurements and determinations were performed on the glass side that had been in contact with the protective gas atmosphere in the course of production. The film texture was assessed using 100-magnification photographs (light microscope MIM-8M). The microstructure was studied using photos (×10,000) obtained with the UEMV-100K electron microscope.

Table 1 shows the number of oxides in the films, the viscosity and surface tension of the two-day FFS. Previously it was suggested that the film structure is built-in in the stage of FFS preparation [2]. In that case, a correlation should exist between the solution viscosity, on one hand, and the intensity and the nature of the distribution of inclusions in the film, on the other hand.

It is seen in Fig. 1 that in the course of going from composition 1 to composition 3, a consecutive increase in crystallization is observed. While in film 1 the microstructure is clearly granular, in film 2 the extended crystalline formations of chain-like and dendritic shapes appear, and in film 3 the dendrite formations are much more pronounced. Accordingly, the microstructure of the film deteriorates significantly and becomes rougher. The viscosity of the respective FFS decreases consecutively from 3.2 to 2.7 mm^2/sec. It can be attributed to a decrease in the concentration of the polymer-forming titanium tetraalkoxide (in this case it is TBT) and modification of the nature of the film inclusions which is probably determined by the size, shape, and number of particles in the disperse phase of the colloidal solution. It is known that the viscosity of any freely disperse system is linearly related to the proportion by volume of the disperse phase. With the proportion by volume of the disperse phase being equal, the viscosity grows with an increase in the degree of dispersion, i.e., with a decrease in the size of the sol

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particles. The viscosity will be lower if the particles are rod-shaped or capable of deformation (flattening or extending) and can acquire an elongated shape [3].

Taking into account these considerations, let us correlate the results in Table 1 with the photos in Fig. 1. Film 1 with a granular structure is obtained from the solution with the highest viscosity in which the proportion by volume of disperse phase should be significant and the particles are probably small [3]. Film 2 contains chain-like inclusions and is obtained from the solution with a lower viscosity. The decrease in viscosity observed may be related to the presence of the rod-shaped or deformable sol particles [3]. The further decrease in the viscosity of the composition 3 FFS and the change in the microstructure of the respective film confirms this assumption.

Film 4 is identical to film 2 in its oxide composition, but another copper-containing material was used in it: cupric nitrate instead of cupric chloride. The film texture underwent a transformation: the number of chain-like crystals decreased significantly and the microstructure changed radically and acquired a clearly granular character as in the film of composition 1 (Fig. 1). Although the fraction of the polymer-forming component in compositions 2 and 4 are equal and the microstructure of films 1 and 4 is identical, the viscosity of FFS of composition 4 is lower than that of FFS of compositions 1 and 2. Hence, the viscosity depends not just on the proportion of the polymer-forming component and the state of the disperse phase, but also on the type of the initial material used to prepare the solution.

Probably the low firing temperature does not facilitate complete decomposition of the copper-containing material to cupric oxide and a certain quantity of Cl^- and NO_3^- anions remains in the sol-gel films, exercising a significant effect on their structure and properties. Thus, the refractive index and the mirror reflection coefficient of film 4 are much lower than those of film 2 [1, 4], which could be attributed to the lower refractive index of cupric nitrate compared to cupric chloride [5].

The textures and microstructures of films 2 and 5 which have the same oxide composition and differ only in the type of the titanium-containing material used for the solutions are very similar. It is just that the inclusions in Film 5 are more branched and its microstructure is rougher than that of Film 2 (Fig. 1). The difference observed may be caused by the different solubilities of cupric chloride in ethanol, acting as the solvent, in all compositions and emerging additionally from TET hydrolysis, and in butanol released in hydrolysis of TBT.

In films of the system considered, the $CaCl_2 \wp 5H_2O$ phase is responsible for the formation of crystals. The greater solubility of these crystals in the ethyl-butyl alcohol mixture is proved by the results of x-ray phase analysis of powders obtained from FFS of compositions 2 and 5; 25 arbitrary units of cupric chloride were discovered in powder 2, and 150 arbitrary units were discovered in powder 5 [1].
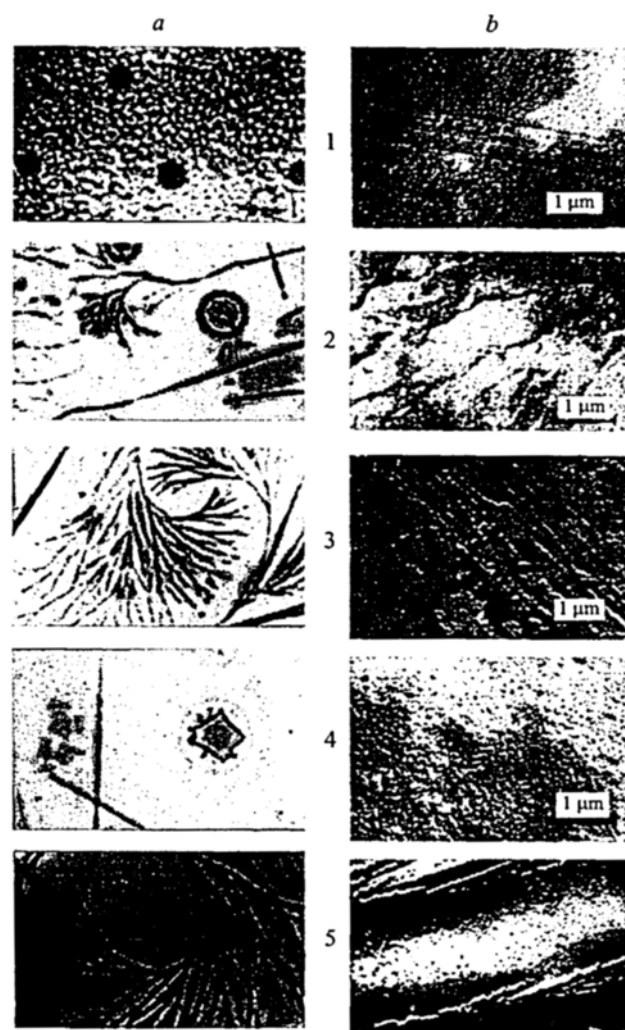

Fig. 1. Photos of films of the CuO – TiO$_2$ system at magnification of 100 (a) and 10,000 (b). 1 – 5) The numbers of the compositions are listed in Table 1.

The enhancement of dendrite-formation is accompanied by an increase in the diffusion reflection factor of film 4 (5.5%) compared to that of film 2 (3.4%). The increase in the degree of particle branching hampers flow of the sol, therefore the viscosity of the FFS of composition 5 is slightly greater than that of composition 2.

In correlating the measurement results for FFS surface tension with the microphotos of the films, it was found that the lowest surface tension is exhibited by compositions 1 and 4 of FFS with rare spheroid particles of disperse phase, since the corresponding films have a granular microstructure (Fig. 1). The surface tension is correlated linearly with the specific surface area of the disperse phase, which is minimal for spherical particles [2]. This is possibly the reason for the low surface tension values of FFS of compositions 1 and 4. Particles of any other shape have a greater surface area, therefore, the surface tension of FFS composition 4 is
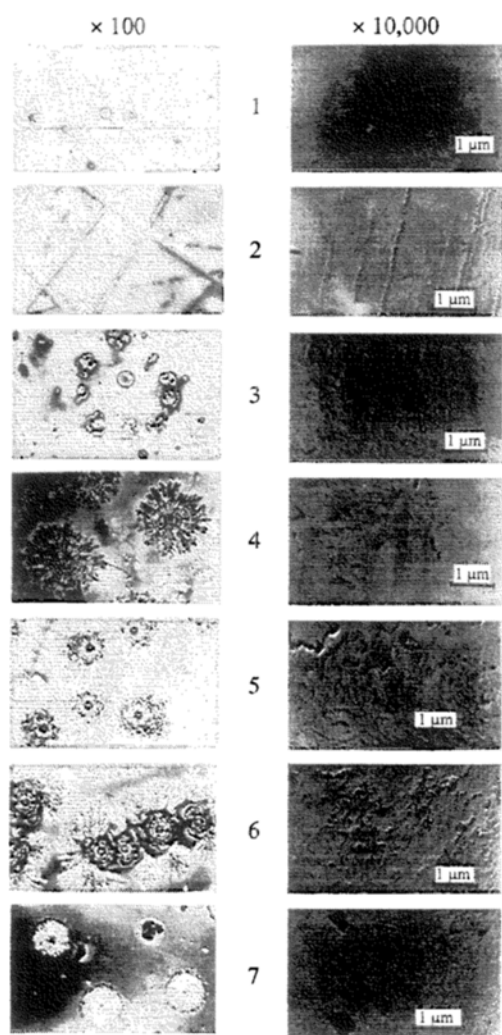
Fig. 2. Photos of films of the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system. 1 – 7) Numbers of the compositions listed in Table 1.

slightly greater than that of composition 1. It is seen in Fig. 1a that in film 4 some chain inclusions are observed along with the spheroid ones.

The maximum surface tension of FFS of composition 5 is due not just to an increase in dendrite formation and roughening of the microstructure, but also to an excess of ethanol in the solution, formed in hydrolysis of TET. Note that in the other FFS the source of titanium dioxide is TBT which produced butanol in hydrolysis. It is known that the surface tension of organic liquids within the same homologous series decreases as the homolog molecular mass increases [6].

Let us divide all cupric-titanium films investigated into two groups by the similarity of their microstructure. The first group includes compositions 1 and 4, and the second includes compositions 2, 3, and 5. In each group the increase in the surface tension of the solution correlates well with the increase in the amount of crystalline phase in the powders obtained from the respective FFS and heat-treated up to 800°C. In spite of the visually significant quantity of inclusions in films 3 and 5 relative to film 2, x-ray phase analysis showed [1] that powder 5 contains the maximum amount of crystalline phase (318 arbitrary units), powder 2 has a smaller amount (273 units), and powder 3 contains only 230 units. It correlates well with the surface tension variation of the respective solutions.

In the $Bi_2O_3 - Fe_2O_3 - TiO_2$ film-forming system, a complicated relationship between the flow parameters of FFS and the composition, texture, and submicrostructure of the film was discovered. The transition from composition 1 to composition 7 is accompanied by a consecutive decrease in the fraction of TiO_2 polymer-forming component in the FFS and in the film. At the same time, the solution viscosity does not change monotonically: the FFS of compositions 3 and 4 have the lowest viscosity, those of compositions 1 and

TABLE 1

Compo-sition	Molar content (%) in film				FFS properties		Material	
	TiO_2	Bi_2O_3	Fe_2O_3	CuO	viscosity, mm^2/sec	surface tension, $10^{-3} N/m$	containing titanium	containing copper
					$CuO - TiO_2$ system			
1	85	—	—	15	3.21	23.0	TBT	Cupric chloride
2	70	—	—	30	2.92	26.5	The same	The same
3	55	—	—	45	2.74	25.2	"	"
4	70	—	—	30	2.87	24.3	"	Cupric nitride
5	70	—	—	30	2.96	28.7	TET	Cupric chloride
					$Bi_2O_3 - Fe_2O_3 - TiO_2$ system			
1	65	10	25	—	2.52	26.2	TET	—
2	55	20	25	—	2.58	25.0	The same	—
3	45	30	25	—	2.28	22.8	"	—
4	35	40	25	—	2.30	24.2	"	—
5	25	50	25	—	2.85	23.7	"	—
6	15	60	25	—	2.88	22.5	"	—
7	5	70	25	—	2.80	22.1	"	—

2 have medium viscosity, and compositions 5, 6, and 7 exhibit the maximum viscosity.

We now correlate the data from Table 1 with the photos shown in Fig. 2. It is known that the viscosity of a disperse system is related proportionately to the proportion by volume of the disperse phase, and the proportion by volume of the disperse phase being equal, the viscosity increases, as the particle size decreases [3]. Therefore, the least homogeneous films 5, 6, and 7 (Fig. 2, ×10,000) are obtained from the most viscous FFS, and the decrease in viscosity of the FFS of composition 7 is correlated with a slight improvement in the microhomogeneity of the film. The minimum viscosity values of the FFS of compositions 3 and 4 correlate with the best microhomogeneity of the films obtained.

The photos of film 1 exhibit no traces of inclusions, i.e., the film is amorphous. This probably ensues from the fact that titanium dioxide is capable of forming amorphous chain aggregates (macromolecules) in colloid solutions. The period of existence of such particles depends on the composition of the disperse system and the age of the sol. These macromolecules impart to the solutions the properties of high-molecular-weight solutions and substantial viscosity (greater than the typical viscosity of a colloidal solution of the same concentration [3]), which agrees with the measurement data on the viscosity of FFS of composition 1.

Similar processes probably cause the high viscosity of FFS of composition 2. Due to a series of internal reasons, the amorphous macromolecules of TiO_2 acquire a crystalline character, which is revealed in the film photos as well as by radiography. According to the data from the x-ray phase analysis, the powder obtained from the FFS of composition 2 and heat-treated up to 400°C contains 65 arbitrary units of TiO_2.

Thus, the viscosity of the solutions investigated in the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system is determined simultaneously by the size and number of the particles, their shapes, and character.

The film composition varies monotonously, which is not so for the variation of their properties and structure. Perhaps, a smooth variation can be expected in the case when all components of the solutions and films are mutually dissolved in each other without reacting and forming complex chemical compounds. Unfortunately, no data on the equilibrium diagram in the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system and the existing three-component compounds could be discovered in the literature. In the $Bi_2O_3 - TiO_2$ and $Fe_2O_3 - TiO_2$ binary systems the following titanates were found: $Bi_2O_3 \cdot 2TiO_2$, $Bi_2O_3 \cdot 3TiO_2$, $Bi_2O_3 \cdot 4TiO_2$, $2Bi_2O_3 \cdot 3TiO_2$, $4Bi_2O_3 \cdot TiO_2$, $12Bi_2O_3 \cdot TiO_2$, $Fe_2O_3 \cdot 3TiO_2$, $2Fe_2O_3 \cdot 3TiO_2$, $Fe_2O_3 \cdot TiO_2$ [7].

We calculated the $Bi_2O_3 : TiO_2$ and $Fe_2O_3 : TiO_2$ ratios in the films investigated and represent their compositions in the form of hypothetical two-component compounds as shown in Table 2. We further correlate the results obtained with the compositions of the two-component iron and bis-

muth compounds listed above. The presence of a third component in the film will undoubtedly change the composition of the compounds, therefore, the further arguments are not rigorous.

The FFS of compositions 3 and 6 gravitate to bismuth titanates, and those of compositions 4 and 5 gravitate to ferric titanates. Fig. 2 shows that films 3 and 6 differ in their microstructure from films 2 and 7, and the large crystals of the regular shape discovered in film 4 are not found in the other films. Note that only the powder of composition 4 obtained from the analogous FFS and heat-treated up to 400°C, only the crystalline phase of Fe_2O_3 was found. Thus, although these data are preliminary, they give reasons for the assumption that a real correlation exists between the film structure and the equilibrium diagram of the respective system.

Neither the surface tension nor the viscosity of the solutions change monotonically in going from composition 1 to composition 7. The FFS of compositions 1 and 2 have the highest surface tension (26.2 × 10^{-3} and 25.0 × 10^{-3} N/m, respectively). This can be attributed to the presence of chain molecules. This assumption does not contradict the results discussed earlier. In the $CuO - TiO_2$ system, the surface tension of the solutions is related proportionately to the number of the chain and dendritic crystals in the films and the amount of the $CuCl_2 \cdot 2H_2O$ crystalline phase responsible for the formation of inclusions of the shapes mentioned [1]. Similar to the $CuO - TiO_2$ system, the appearance of spherical or spheroid inclusions in films of the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system (compositions 3 – 7) correlates with a decrease in the FFS surface tension to 24.2 × $10^{-3} - 22.1 × 10^{-3}$ N/m. It is known that the surface tension of any sol depends on the surface energy of the disperse phase, and this phase is related linearly to the total particle surface area [3, 8].

Let us take the shape, size, and amount of the disperse phase in the FFS analyzed to be close to the inclusion parameters discovered in the respective films. According to the formula

$$S = \pi D^2,$$

where S is the surface area of the inclusions, $\pi = 3.14$, and D is the average inclusion diameter, based on the crystal dimen-

TABLE 2

Composition	Bismuth titanates	Ferric titanates
1	$Bi_2O_3 \cdot 6,7TiO_2$	$Fe_2O_3 \cdot 2,6TiO_2$
2	$Bi_2O_3 \cdot 2,7TiO_2$	$Fe_2O_3 \cdot 2,2TiO_2$
3	$2Bi_2O_3 \cdot 3TiO_2$	$Fe_2O_3 \cdot 1,8TiO_2$
4	$1.1Bi_2O_3 \cdot 5TiO_2$	$2Fe_2O_3 \cdot 2,8TiO_2$
5	$2Bi_2O_3 \cdot TiO_2$	$Fe_2O_3 \cdot TiO_2$
6	$4Bi_2O_3 \cdot TiO_2$	$1.6Fe_2O_3 \cdot TiO_2$
7	$13Bi_2O_3 \cdot TiO_2$	$12Fe_2O_3 \cdot TiO_2$

sions appraised by the photos (Fig. 2, × 100) and their quantity in the field of vision, we determine the total surface area of the disperse phase. The inclusions of film 4 (5300 mm^2) turn out to have the largest surface area. Perhaps that is why the corresponding solution has the highest surface tension $(24.2 \times 10^{-3}$ N/m)

However, the variation in the surface tension cannot be explained just by the shape of the disperse phase and its surface energy. Evidently, the capability of the sol particles to react to each other, producing new chemical compounds, plays an important role. This assumption is supported by the correlation between the solutions and the films of compositions 5 and 7. The surface area of the inclusions in film 5 (2340 mm^2) is less than in film 7 (2570 mm^2), and the surface tension of the FFS of composition 5 is, on the contrary, greater than that of composition 7 $(23.7 \times 10^{-3}$ and 22.1×10^{-3} N/m, respectively). It can be attributed to the fact that composition 5 seems to gravitate to one of the actually existing iron titanates, and composition 7 gravitates to bismuth titanate. It can be assumed that iron titanates enhance and bismuth titanates reduce the surface tension of the solution. In that case the high surface tension of FFS composition 4 is partly due to the fact that it is close to the $2Fe_2O_3 \cdot 5TiO_2$ compound, and compositions 3 and 6 gravitate to bismuth titanates, and therefore, the surface tension of the respective solutions is slightly lower.

Thus, the viscosity of the copper-titanium solutions investigated depends on the volume fraction of disperse phase and is closely related to the particle shape. Spherical particles increase the viscosity, and chain and dendritic particles reduce it. The appearance of branched (dendrite) inclusions in films of the $CuO - TiO_2$ system is associated with the presence of $CuCl_2 \cdot 2H_2O$ and is caused by the incomplete decomposition of cupric chloride during firing of the film. The intensity of dendrite formation depends on the solubility of $CuCl_2 \cdot 2H_2O$ in different environments.

The surface tension of the solutions is determined by the nature of the solvent and is correlated proportionately with the surface area of the disperse phase. It is minimal if the particles are spherical (or spheroid) and increases when the sol particles are transformed into chain and (or) dendritic particles.

The microinhomogeiety of films of the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system is related to the FFS viscosity. The emergence of amorphous macrochain aggregates of TiO_2 significantly increases the viscosity. The properties of these solutions and films do not change monotonically due to the reaction between the components and ensuing formation of complexes. The phase equilibrium diagram probably has a significant effect on the chemical interaction determining the composition and the structure of the compounds formed in FFS and films and, consequently, on the microstructure of the films and the surface tension of the solutions.

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